

Final Performance Report

Project Title:

Spin Injection and Its Effects on Lasing Action in Conjugated Polymers

This project specifically focuses on two particular topics: (i) developing organic spintronics for magnetically controlling constructive and non-constructive interaction of excited processes towards lasing applications and (ii) elucidating singlet and triplet photovoltaic processes towards improving photovoltaic efficiencies in organic solar cells.

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Agreement Number:

FA9550-06-1-0070

20100721048

REPORT DOCUMENTATION PAGE

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Executive Service Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

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1. REPORT DATE (DD-MM-YYYY) 16-06-2009		2. REPORT TYPE Final Technical		3. DATES COVERED (From - To) 01 Feb 2006 - 30 Nov 2008	
4. TITLE AND SUBTITLE Spin Injection and Its Effects on Photovoltaic Response and Lasing Action in Conjugated Polymers				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA9550-06-1-0070	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Bin Hu				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Materials Science and Engineering 608 Dougherty Engineering Building University of Tennessee Knoxville, TN 37996				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 875 N Randolph St Suite 325 Arlington, VA 22203 RSL				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR/RSA	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution A: Unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The objective is to improve photovoltaic efficiency and lasing action in conjugated polymers by using spin polarization. Specifically, photoinduced spin transfer from ferromagnetic nanowires and electrical spin injection from nanoscale ferromagnetic electrode will be used in photovoltaic cells and lasing devices, respectively, to control the singlet/triplet exciton formation and excitonic dynamic processes for the enhancements of exciton dissociation and optical gain.					
15. SUBJECT TERMS "spin injection" -- "photovoltaic response" -- "conjugated polymers"					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Unlimited	18. NUMBER OF PAGES 18	19a. NAME OF RESPONSIBLE PERSON
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (Include area code)

I. Objectives:

The project seeks to investigate the effects of magnetic field and spin injection on constructive and non-constructive interactions of singlet and triplet excited states in organic semiconducting polymers. The goal is to provide new understanding and new methodology for controlling coherent and incoherent excited processes for lasing and photovoltaic applications by magnetically elucidating exciton-exciton and exciton-charge interactions.

This project has two particular impacts. First, the spin injection and magnetic field effects can form a new principle to develop magnetically enhanced next-generation organic semiconductor devices for lasing and photovoltaic applications. Second, the spin injection and magnetic field effects can experimentally visualize spin-dependent excited processes critically occurring in organic semiconducting materials but challenging to measure by conventional experiments. As a result, the studies of spin injection and magnetic field effects are crucially important for both organic optoelectronics and spintronics.

II. Status of Effort:

Significant progress has been made in (1) realizing spin injection, (2) discovering positively and negatively tunable magnetoresistance towards magnetically controlling constructive and non-constructive excited processes, (3) discovering tunable magnetic field dependence of electroluminescence towards developing organic spintronics for magnetically controlling coherent and incoherent electronic processes, (4) revealing singlet and triplet photovoltaic processes, (5) demonstrating triplet enhanced photovoltaic efficiencies, and (6) elucidating the underlying mechanism of triplet enhanced photovoltaic response, and (7) discovering magnetic field dependence of photoluminescence based on inter-molecular excited states towards developing organic spin-optics. These achievements have established solid foundations to develop organic spintronics and to use magnetic field and spin injection for controlling coherent and incoherent excited processes towards lasing development. On the other hand, these achievements have developed unique experimental tools to visualize useful and non-useful excited processes in organic solar cells and therefore provide unique methodologies and new guidelines to control to improve organic photovoltaic efficiencies.

2.1 Discovery of Novel Approach for Spin Injection

We discovered a novel approach, using *ferromagnetic nano-dot electrode*, to obtain efficient spin injection in organic semiconducting polymer thin films [Yue Wu and Bin Hu, *Phys. Review B*, **75**, 075213 (2007)]. We found that the ferromagnetic cobalt nano-dot electrode can provide highly efficient spin injection up to 55% into poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEHPPV). The diffusion length of injected spin-polarized holes was determined to be about 60 nm. This discovery has solved the long-time challenge: extremely low spin injection efficiency in polymer thin films. Therefore, this discovery makes it possible to generate significant spin-polarized excited states and to investigate how spin-polarized excited states experience optical gain in organic semiconducting materials.

2.2 *Discovery of Unique Magnetoresistance Tunable between Positive and Negative Values towards Controlling Constructive and Non-Constructive Excited Processes*

We discovered that both positive and negative magnetic field effects can be obtained in organic semiconducting materials [Yue Wu and Bin Hu, *Nature Materials*, 6, 985, 2007]. This discovery has two important impacts. First, the positive and negative magnetic field effects can be used to develop magnetically controllable organic semiconductor devices by using non-magnetic organic semiconducting materials. Second, the discovered positive and negative magnetic field effects form an effective experimental method to visualize the useful and non-useful excited processes in lasing and photovoltaic devices. Specifically, positive magnetic field effects can be observed when constructive interaction occurs between excited states. When non-constructive interaction occurs between excited states and charge carriers, negative magnetic field effects can be shown. Because constructive and non-constructive interactions are very important excited processes in lasing and photovoltaic devices, the positive and negative magnetic field effects will impact the lasing and photovoltaic research.

2.3 *Discovery of Positively and Negatively Tunable Electroluminescence towards Development of Magnetic Field Effects-Based Organic Spintronics*

We recently demonstrated that electroluminescence dependence of magnetic field can be tuned between positive and negative values in non-magnetic organic semiconducting materials (to be published). This experimental demonstration indicates that magnetic field effects of excited states can be used to develop organic spintronics without using spin injection. Especially, this demonstration shows that the use of magnetic field effects provides an alternative approach to develop organic spintronics based on non-magnetic materials, as compared to delicate spin injection-based organic spintronics that requires superior magnetic materials.

2.4 *Discovery of Detailed Singlet and Triplet Photovoltaic Processes in Organic Solar Cells*

We established an effective experimental approach, using *magnetic field dependence of photocurrent*, to investigate singlet and photovoltaic processes intrinsically occurring in organic solar cells [*Advanced Functional Materials*, **18**, 2611 (2008); *Appl. Phys. Lett.* **89**, 131116 (2006)]. For the first time, we demonstrated that three photovoltaic channels occurring in organic solar cells: dissociation in polaron-pair states, charge reaction in excitonic states, and dissociation in inter-molecular charge-transfer states. Especially, the magnetic field dependence of photocurrent shows how donor-acceptor interaction affects these three photovoltaic channels. This provides critical understanding about how photovoltaic processes should be controlled towards the improvement of photovoltaic efficiencies. Specifically, weak donor-acceptor interaction dissociates low-binding-energy polaron pairs. Large-binding-energy excitons undergo charge reaction and dissociate into free charge carriers. Reducing the formation of charge-transfer complex states requires sufficient electron and hole transport channels. These critical understanding provide new guidelines to design more efficient photovoltaic polymers and devices.

2.5 Triplet Enhanced Photovoltaic Response

We found that triplet excitons can give rise to more efficient photocurrent in organic semiconducting materials [*Appl. Phys. Lett.* **89**, 131116 (2006)]. This experimental finding indicates that heavy-metal complex organic materials have potential applications in organic solar cells. Recently, our magnetic studies of triplet-generated photocurrent show that the strong electrical polarization associated with heavy-metal complex structures in triplet materials is responsible reason why triplet excitons can generate more efficient photocurrent (to be published). Specifically, the strong electrical polarization associated with heavy-metal complex structures can effectively dissociate triplet excitons and consequently generate more efficient photocurrent. This finding elucidates why polythiophene polymer, in which the triplet fraction is as high as 70%, is a better choice for photovoltaic application. On the other hand, this finding provides critical information about how internal electrical polarization should be considered to design better photovoltaic polymers.

2.6 Discovery of Underlying Mechanism of Triplet Enhanced Photovoltaic Response

Based on the studies of magnetic field dependence of photocurrent, we recently discovered that triplet enhanced photovoltaic response comes from the locally enhanced dielectric field caused by heavy-metal complex structures in the generation of triplet excitons (to be published). This discovery revealed why triplet excitons can generate more efficient photocurrent as compared to singlet excitons. Especially, this discovery provides a new guideline to develop advanced photovoltaic polymers and design more efficient solar cells.

2.7 Development of Organic Spin-Optics towards Magnetically Controlling Coherent and Incoherent Optical Processes

There has been a great challenge to develop organic spin-optics due to the fact that (i) photoexcitation does not generate spin polarization. This challenge makes photoluminescence *insensitive* to an external magnetic field in organic semiconducting materials. We recently found that the photoluminescence from inter-molecular excited states can show significant magnetic field dependence under normal photoexcitation (to be published). This experimental finding provides principle to develop organic spin-optics by using light-emitting inter-molecular excited states. Especially, this finding indicates that coherent and incoherent processes in inter-molecular excited states can be, in principle, controlled by an external magnetic field.

III. Accomplishments/New Findings

The project accomplishments include new discoveries and unique demonstrations in both organic spintronics, towards magnetically controlling coherent and incoherent excited processes, and photovoltaics, towards developing new understanding to develop efficient organic solar cells.

3.1 *Discovery of Highly Efficient Spin Injection from Nano-Dot Ferromagnetic Electrode¹*

We demonstrated, for the first time, that nano-dot ferromagnetic cobalt (Co) electrode can provide highly efficient spin injection up to 55%. The spin injection efficiency dramatically decreases with increasing Co dot size (Fig. 1). The realization of spin injection in organic semiconducting polymer thin films has been a long-time challenge because of (i) rough surface of polymer thin films prepared by spin coating and (ii) insufficient Schottky barrier to overcome the critical obstacle for spin injection: conductivity mismatch between ferromagnetic electrode and polymer film. Our discovery presents a novel strategy by using nano-dot ferromagnetic electrode to respond to this long-time challenge in achieving spin injection in organic semiconducting polymers. The nano-dot ferromagnetic electrode can form high-quality nanoscale Schottky ferromagnetic/polymer interfaces that dramatically facilitate the spin transport from ferromagnetic electrode to semiconducting polymer. As a result, our discovery of using nano-dot ferromagnetic electrode paves a solid roadway to investigate spin-polarized singlet and triplet excited states towards the goal of magnetically increasing optical gain of organic lasing polymers¹.

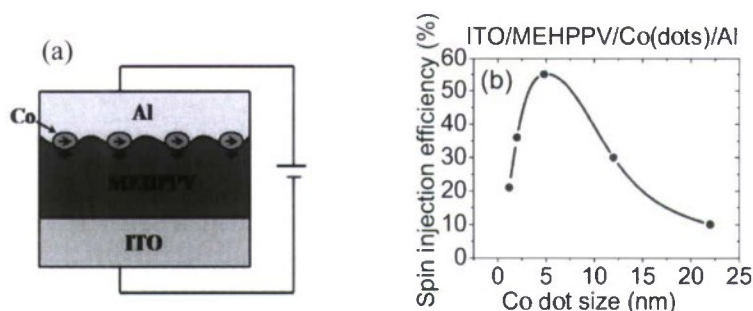


Fig. 1 (a) Co nano-dot electrode for spin-polarized hole injection.
(b) Spin injection efficiency as a function of Co dot size.

3.2 *Discovery of Positive and Negative Magnetic Field Effects for Development of Magnetoresistance Based on Constructive and Non-Constructive Excited Processes²*

An external magnetic field can affect the constructive and non-constructive interactions of singlet and triplet excited states through changing spin polarization in organic semiconducting materials. However, the unclear underlying mechanism of magnetic field effects forms a great challenge in using magnetic field effects to experimentally visualize the constructive and non-constructive interactions of singlet and triplet excited states. Our recent publication (Nature Materials) has revealed that the magnetic field effects (magnetoresistance) can be tuned between positive and negative values if the exciton dissociation and exciton-charge reaction are changed

by adjusting electron and hole bipolar charge injection. Fig. 2 shows this unique tuning of magnetic field effects (magnetoresistance) by using a simple double-layer light-emitting device design in two example polymers: poly(N-vinylcarbazole) (PVK) and poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylenc] (MEHPPV). This discovery provides a fundamental mechanism to use magnetic field effects for the investigation of the constructive and non-constructive interactions of singlet and triplet excited states towards the goal of magnetically enhancing photovoltaic and lasing responses in organic semiconducting materials².

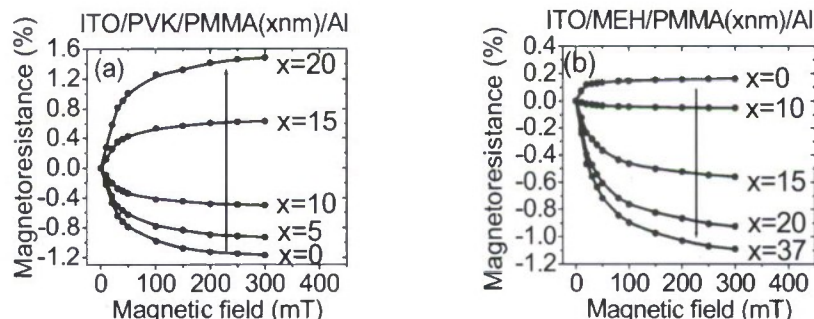


Fig. 2 Tuning magnetic field effect (magnetoresistance) between positive and negative values by controlling dissociation and charge reaction in excited states through adjusting PMMA layer thickness and the resultant bipolar electron and hole injection in double-layer light-emitting diodes.

(a) Tuning negative magnetic field effect to positive value.

(b) Tuning negative magnetic field effect to negative value.

3.3 Visualization of Singlet and Triplet Photovoltaic Processes in Organic Solar Cells³

It is known that sunlight absorption generates both singlet and triplet excitons in photovoltaic polymers such as poly(3-methylthiophene) (P3HT). However, it has been unclear that how singlet and triplet excitons convert into photocurrent in organic solar cells. Particularly, insufficient understanding of singlet and triplet photovoltaic processes has been an obstacle in improving photovoltaic efficiencies. We have developed a unique experiment: magnetic field dependence of photocurrent to visualize both singlet and triplet photovoltaic processes. Specifically, we observed three photovoltaic channels: singlet exciton dissociation, triplet-exciton-charge reaction, and the dissociation of charge-transfer complex states. Clearly, singlet and triplet photovoltaic processes give rise to positive and negative responses at low magnetic field (< 150 mT), respectively (Fig. 3). In addition, at high magnetic field (> 150 mT) the positive magnetic response indicates that the dissociated electrons and holes form bound electron-hole pairs, namely charge-transfer complex states. *This is the first experimental visualization of detailed singlet and triplet photovoltaic processes in organic solar cells³.* We discovered that singlet and triplet excitons undergo dissociation and charge reaction, respectively, to generate photocurrent in organic semiconducting materials. In organic solar cells, we found that the donor-acceptor interaction can directly dissociate both singlet and triplet excitons but generates bound electron-hole pairs, namely charge-transfer complex states, at the donor-acceptor interfaces. The charge-transfer complex states form a serious loss in the generation of

photocurrent in organic solar cells. Effectively controlling the charge-transfer complex states becomes a critical issue to improve the photovoltaic efficiencies. We further found that the form of charge-transfer complex states depends on localized dielectric field and charge mobilities. This experimental finding provides a new guideline to control the charge-transfer complex states towards the improvement of photovoltaic efficiencies.

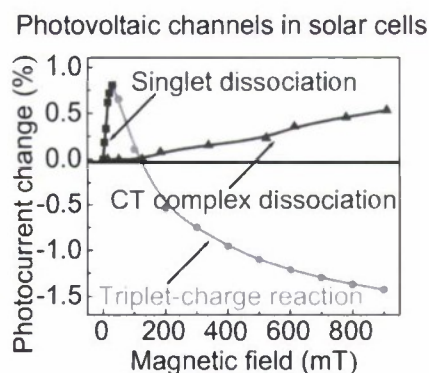


Fig.3 Visualization of detailed photovoltaic channels: (i) singlet exciton dissociation (positive response at low magnetic field < 50 mT), (ii) triplet exciton-charge reaction (negative response at low magnetic field < 150 mT), (iii) dissociation of charge-transfer complex states (positive response at high magnetic field > 150 mT) in organic solar cells.

3.4 Triplets versus Singlets in Photovoltaic Response in Organic Solar cells⁴

It has been a big question whether triplet excitons can enhance photovoltaic response in organic solar cells due to their large binding energies. We found that triplet excitons can indeed show a more efficient photocurrent as compared to singlet excitons⁴ (Fig. 4). *This is the first demonstration that triplet excitons can be used to enhance organic photovoltaic response.*

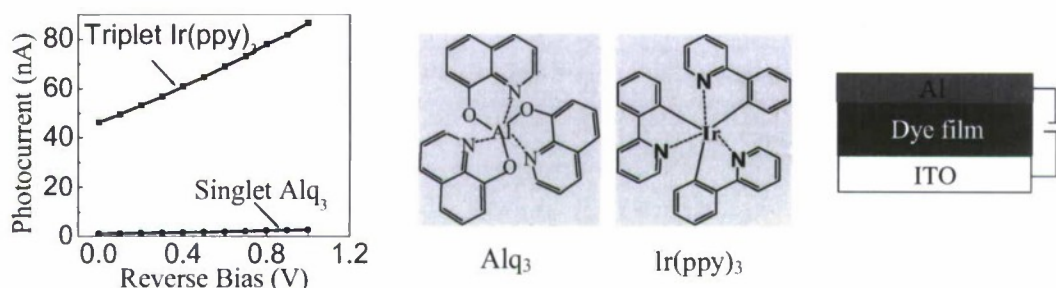


Fig. 4 Photocurrent from singlet Alq₃ and triplet Ir(ppy)₃.

This demonstration was successfully made by selecting two particular organic semiconducting molecules: Alq₃ and Ir(ppy)₃, which have similar LUMO (lowest unoccupied molecular orbital), HOMO (highest occupied molecular orbital), charge mobilities, absorption spectrum, and absorption coefficient. However, the singlet and triplet exciton ratios are very different: triplet

fractions⁵ in Alq₃ and Ir(ppy)₃ are 20% and 100%, respectively. This demonstration clearly shows that triplet excitons can be used to generate efficient photocurrent.

3.5 Triplet Enhanced Photovoltaic Efficiency⁶

Based on our discovery that triplet exciton can generate efficient photocurrent, we successfully improved photovoltaic efficiency by further increasing triplet exciton density through dispersing Ir(ppy)₃ molecules into P3HT:PCBM solar cell. The photovoltaic power efficiency was increased by 20% from 4.0% to 4.8% by adjusting singlet and triplet photovoltaic contributions⁶ (Fig. 5).

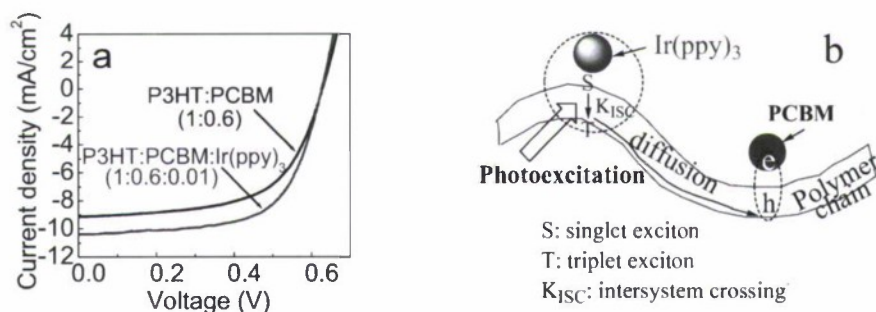


Fig. 5. (a) Photovoltaic enhancement by adjusting singlet and triplet contributions through adding Ir(ppy)₃ molecules in organic solar cell of ITO/PEDOT/P3HT+PCBM+Ir(ppy)₃/Al. (b) Schematic process to show long-diffused triplet excitons to donor-acceptor interface for dissociation.

The triplet enhanced photovoltaic efficiency includes three important processes: (i) dispersed Ir(ppy)₃ molecules increase the triplet exciton fraction in P3HT matrix, (ii) triplet excitons can more effectively diffuse to donor-acceptor interfaces for dissociation, and (iii) heavy-metal complex structures in the Ir(ppy)₃ increase internal dielectric field to enhance exciton dissociation.

3.6 Discovery of Underlying Mechanism of Triplet Enhanced Photovoltaic Response⁷

It has been experimentally found that triplet excitons can generate more efficient photocurrent⁴. However, the *underlying mechanism is not clear*. We recently used unique magnetic field dependence of photocurrent and discovered that the heavy-metal complex structures used to generate triplet excitons are responsible for triplet enhanced photocurrent. Specifically, the heavy-metal complex structures in generating triplet excitons can largely increase internal dielectric field and consequently enhance exciton dissociation. This discovery indicates that internal dielectric field is critical important in exciton dissociation towards the improvement of photovoltaic efficiency.

Fig. 6 clearly shows that dispersing Ir-65 heavy-metal complex reduces the positive magnetic field dependence of photocurrent, which is the signature of increasing exciton dissociation in organic semiconducting polymer: poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO). This heavy-metal complex enhanced exciton dissociation is very similar to the donor-acceptor interaction

enhanced exciton dissociation, revealed by the reduction of positive magnetic field dependence of photocurrent (see the comparison between Ir-65 dye-related magnetic field effects of photocurrent and PCBM-related magnetic field effects of photocurrent). On the other hand, both Ir-65 dye [Iridium (III) bis(2-(4,6-difluorophenyl)pyridinato-N,C2)] and PCBM doping can largely increase the photocurrent (Fig. 7).

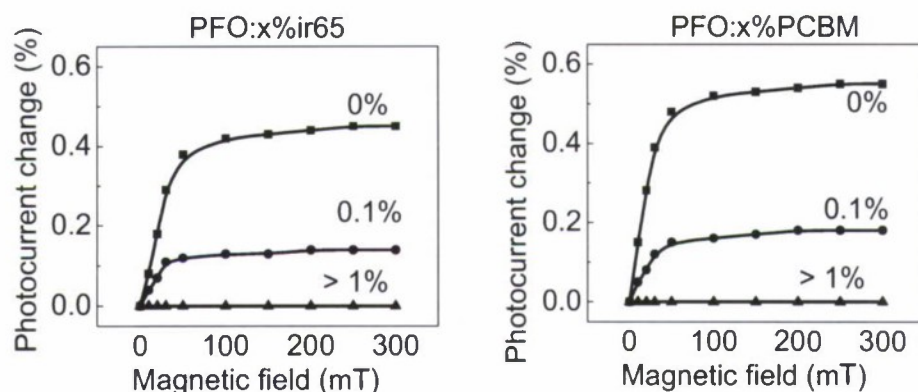


Fig. 6 Ir-65 dye and PCBM effects on magnetic field dependence of photocurrent. Doping ($> 1\%$) of heavy-metal complex Ir-77 and PCBM completely dissociates singlet excitons in poly(9,9-dioctylfluorenyl-2,7-diyl).

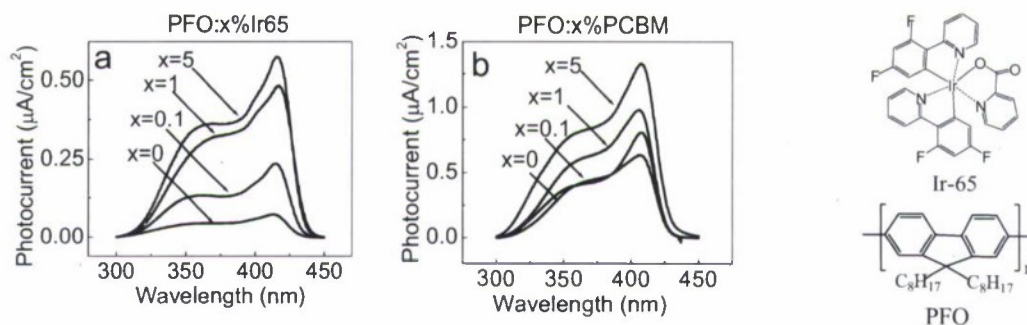


Fig. 7 Photocurrent spectrum for Ir-65 and PCBM doped PFO system. The photocurrent largely increases with Ir-65 and PCBM doping due to enhanced exciton dissociation.

Nevertheless, our studies of magnetic field dependence of photocurrent have revealed that heavy-metal structures enhanced exciton dissociation through dielectric field is the reason why triplet excitons can generate more efficient photocurrent. Especially, this discovery presents a new guideline to develop advanced photovoltaic polymers and design more efficient solar cells.

3.7 Discovery of Tunable Magnetic Field-Dependent Electroluminescence for Development of Magnetic Field Effects-Based Organic Spintronics⁸

We discovered that a low magnetic field can change organic electroluminescence with positive or negative sign in non-magnetic organic semiconducting materials. This discovery demonstrates a new and convenient method to develop organic spintronics based on magnetic field effects of excited states without using difficult spin injection.

Fig. 8 a shows that magnetic field dependence of electroluminescence can be changed between positive and negative values when the bipolar injection is adjusted towards the balanced and unbalanced states of bipolar injection, respectively, by using thin PMMA insulating layer thickness. This is the first experimental demonstration to show positively and negatively tunable magnetic field dependence of electroluminescence from non-magnetic organic semiconducting materials. This demonstration provides a guideline to develop organic spintronics based on magnetic field effects in non-magnetic organic semiconducting materials.

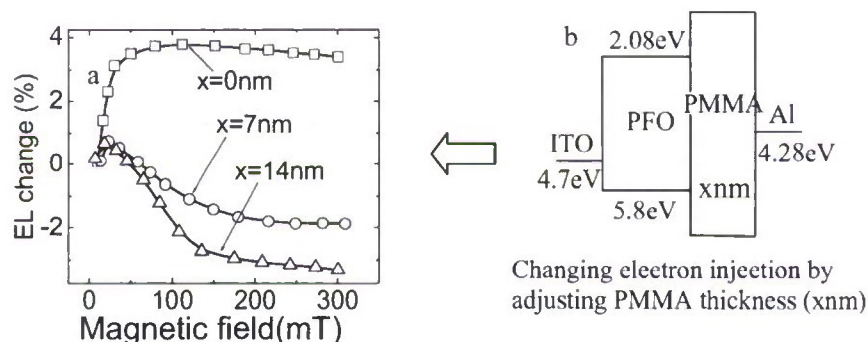


Fig. 8 a: Changing magnetic field dependence of electroluminescence between positive and negative values by adjusting electron injection towards unbalanced bipolar injection. b: Band diagram for tuning bipolar injection by using thin insulating layer.

3.8 Discovery of Magnetic Field-Sensitive Photoluminescence to Develop Organic Spin-Optics⁹

It has been a great challenge to demonstrate spin-optics based on organic semiconducting materials. This is because (i) photoluminescence is not sensitive applied magnetic field and (ii) optical excitation can not realize spin injection. We recently found that light-emitting inter-molecular excited states, namely exciplex states, can have significant response to a low magnetic field. This experimental funding makes it possible, for the first time, to develop organic spin-optics.

Our experimental funding is summarized in Fig. 9 for the inter-molecular excited states (exciplex states) formed between TPD and BBOT in PMMA matrix. It can be clearly seen that the photoluminescence from inter-molecular exciplex states is significantly sensitive to applied magnetic field: the photoluminescence rapidly increases with magnetic field and then becomes

saturated at the field of 100 mT. However, the photoluminescence from pure TPD and BBOT shows complete independence of magnetic field. Clearly, *this experimental discovery indicates that organic spin-optics can be developed based on light-emitting inter-molecular excited states by using organic semiconducting materials.*

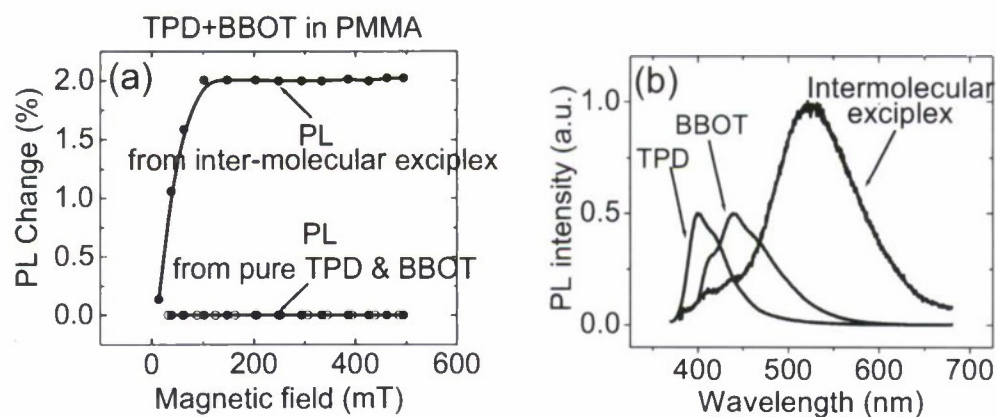


Fig. 9 Positive magnetic field dependence of photoluminescence (PL) for inter-molecular excited states (exciplex states). Note, the photoluminescence from pure TPD and BBOT shows complete independence of magnetic field.

I.V. Personnel Supported:

1. Yue Wu, Ph.D student with full support (from November, 2005 to August, 2007)

Yue Wu has been focusing on the studies of organic spintronics towards magnetically controlling coherent and incoherent excited processes in organic semiconducting materials during his Ph.D study.

Yue Wu was graduated in August, 2007 with Ph.D degree. He was then become a postdoc researcher at UCLA (Yang Yang's group). Yue Wu is now working at Solarmer Inc. on organic solar cells.

2. Zhihua Xu, Ph.D student with full support (from February, 2006 to September, 2008)

Zhihua Xu has been focusing on the studies of singlet and triplet photovoltaic processes towards improving photovoltaic efficiencies in organic solar cells during his Ph.D study.

Zhihua Xu was graduated in September, 2008. Zhihua Xu is now working at Brookhaven National Lab on organic electronics.

3. Ming Shao, Ph.D student with full support since August, 2007

Ming Shao has been focusing on the study of organic spintronics towards lasing applications.

4. Liang Yan, Ph.D student with full support since August, 2008

Liang Yan is currently studying (i) the effects of internal dielectric field on photovoltaic response in triplet-based organic solar cells and (ii) the improvement of photovoltaic efficiencies by using triplet states and internal dielectric field.

V. Publications from November 2005 to September 2008:

Published papers:

1. Photovoltaic Processes of Singlet and Triplet Excited States in Organic Solar Cells
Zhihua Xu and Bin Hu
Adv. Func. Mater. **18**, 2611-2617, 2008
2. Review article: Solar Energy-Conversion Processes in Organic Solar Cells
Zhihua Xu, Huidong Zang, and Bin Hu*
JOM (Journal of the Minerals, Metals and Materials Society), September, in press, 2008
3. Improvement of Photovoltaic Response Based on Enhancement of Spin-Orbital Coupling and Triplet States in Organic Solar Cells
Zhihua Xu, Bin Hu*, and Jane Howe
J. Appl. Phys. **103**, 043909 (2008) (Selected for March 10, 2008 issue of Virtual Journal of Nanoscale Science & Technology)
4. Tuning magnetoresistance between positive and negative values in organic semiconductors
Bin Hu* and Yue Wu
Nature Materials, **6**, 985 (2007)
5. Application of NaYF₄:Yb,Er upconversion fluorescence nanocrystals for solution-processed near infrared photodetectors
Cheng-Jun Sun, Zhihua Xu, Bin Hu, G. S. Yi, G. M. Chow, and Jian Shen
Appl. Phys. Lett. **91**, 191113 (2007)
6. Enhancement of quantum efficiency of organic light emitting devices by doping magnetic nanoparticles
Cheng-Jun Sun, Yue Wu, Zhihua Xu, Bin Hu*, Jianmin Bai, Jian-Ping Wang, Jian Shen
Appl. Phys. Lett. **90**, 232110 (2007)
7. Tuning Magnetoresistance and Magnetic Field-Dependent Electroluminescence through Mixing Strong-Spin-Orbital-Coupling Molecule and Weak-Spin-Orbital-Coupling Polymer
Yue Wu, Bin Hu*, and Jane Howe
Phys. Rev. B, **75**, 035214 (2007)
8. Spin Injection from Cobalt Nanodot Electrode in conjugated Polymers
Yue Wu, Anping Li, Jane Howe, Jian Shen, and Bin Hu*
Phys. Review B, **75**, 075213 (2007) (selected for February 26, 2007 issue of Virtual Journal of Nanoscale Science & Technology)
9. Spin Injection from Cobalt Nanodot Electrode in conjugated Polymers
Yue Wu, Anping Li, Jane Howe, Jian Shen, and Bin Hu*
Virtual Journal of Nanoscale Science & Technology, February, 26, (2007)
10. Improvement of Photovoltaic Response Based on Spin-Orbital Coupling Increased Triplet States in Organic Solar Cells
Zhihua Xu and Bin Hu*
MRS proceeding (Boston 2006)
11. Metal Electrode Dependent Magnetoresistance in Organic Semiconductor Devices
Yue Wu and Bin Hu*
MRS proceeding (Boston 2006)
12. Metal Electrode Effects on Spin-Orbital Coupling and Magnetoresistance in Organic Semiconducting Materials

Yue Wu and Bin Hu*

Appl. Phys. Lett. **89**, 203510 (2006)

13. Dissociation Processes of Singlet and Triplet Excitons in Organic Photovoltaic Cells
Zhihua Xu, Yue Wu, and Bin Hu*
Appl. Phys. Lett. **89**, 131116 (2006)
14. Ferromagnetic Nanowire Effects on Singlet and Triplet Exciton Fractions in Fluorescent and Phosphorescent Organic Semiconductors
Bin Hu*, Yue Wu, Zongtao Zhang, Sheng Dai, and Jian Shen
Appl. Phys. Lett. **88**, 022114(2006)

To be published papers

1. Triplet Enhanced Photovoltaic Response in Organic Solar Cells
Zhihua Xu and Bin Hu, under review in *Appl. Phys. Lett.*
2. Heavy-metal Structures Effects on Exciton Dissociation in Organic Solar Cells
Zhihua Xu and Bin Hu, to be published
3. Tuning Magnetic Field Dependence of Electroluminescence in Non-Magnetic Organic Semiconducting Materials
Ming Shao, Liang Yan, and Bin Hu, to be published
4. Magnetic Field-Dependent Photoluminescence Based on Inter-Molecular Excited States
Liang Yan, Ming Shao, and Bin Hu, to be published

Interactions and Transitions:

a. Presentations at Conferences

Invited Presentation

- (1) **Magnetic Responses in Organic Light-Emitting Diodes and Solar Cells**
Bin Hu
International Symposium on Materials for Enabling NanoDevices
Tainan, Taiwan, September 03-05, 2008
- (2) **Positive and Negative Magnetic Field Effects in Organic Semiconductors**
Bin Hu
International Conference on Science and Technology of Synthetic Metals, Pernambuco, Brazil, July 06 -11, 2008
- (3) **Spin Injection and Magnetoresistance in Organic Semiconductors**
Bin Hu
LEOS (Laser Electro-Optics Society) Conference, Orlando, FL, October 22, 2007
- (4) **Magnetic Field Effects in Organic Semiconductors**
Bin Hu
Department of Physics, University of Rochester, Rochester, NY, October, 2007
- (5) **Spin-Orbital Coupling and Magnetoresistance Tuning in Organic Semiconductors**
Bin Hu
APS Meetings, Denver, CO, March 09, 2007

Oral Conference Presentation

(1) Tuning magnetoresistance in Organic Semiconductors

Bin Hu

Workshop on Spintronic Effects in Organic Semiconductors

Bologna, Italy, September 09-12, 2007

(2) Research and Education in Energy-Technological Plastic Materials

Bin Hu

Coalition of National Science Funding at Capital Hill, Washington DC, July 26, 2007

(3) Improvement of Photovoltaic Response Based on Enhancement of Triplet States in Organic Solar Cells

Bin Hu

MRS meeting, Boston, November 2006

(4) Spin-Orbital Coupling Effects on Magnetoresistance in Organic Materials

Bin Hu

International Conference of Synthetic Metals, July 02 – 08, 2006, Dublin, Ireland

b. Consultative and advisory functions

None.

c. Transitions

None.

V. New Discoveries

- (1) Highly efficient spin injection from ferromagnetic nano-dot electrode has been discovered towards magnetically enhancing optical gain in lasing polymers.
- (2) Unique tuning of magnetic field effects with positive and negative values has been discovered towards the magnetic control of constructive and non-constructive interactions of singlet and triplet excited states.
- (3) Positively and negatively tunable magnetic field dependence of electroluminescence has been obtained for the development of organic spintronics.
- (4) Detailed singlet and triplet photovoltaic channels have been experimentally visualized by using magnetic field effects of photocurrent. The photovoltaic efficiency has been improved by adjusting singlet and triplet photovoltaic processes in bulk-heterojunction organic solar cells.
- (5) Triplet enhanced photovoltaic response has been demonstrated for the first time in organic semiconducting materials.
- (6) The underlying mechanism of triplet enhanced photovoltaic response has been elucidated. We found that the local dielectric field caused by heavy-metal complex structures in generating triplet excitons is responsible for triplet enhanced photovoltaic response.
- (7) It has been discovered that photoluminescence from inter-molecular excited states can show significant magnetic field dependence. This discovery makes it possible to develop organic spin-optics.

No patent was filed yet.

V.I. Honors/Awards:

- (i) NSF Career Award – February 2007
National Science Foundation
- (ii) Chancellor's Research and Creative Achievement Professional Promise Award–April 2008
University of Tennessee
- (iii) Research Fellow Award – April 2008
College of engineering
University of Tennessee
- (iv) Faculty Award for Excellence in Research – April 2008
Department of Materials Science and Engineering
University of Tennessee

References

- ¹ Spin Injection from Cobalt Nanodot Electrode in conjugated Polymers
Yue Wu, Anping Li, Jane Howe, Jian Shen, and Bin Hu*
Phys. Review B, 75, 075213 (2007)
- ² Tuning magnetoresistance between positive and negative values in organic semiconductors
Bin Hu* and Yue Wu
Nature Materials, 6, 985 (2007)
- ³ Photovoltaic Processes of Singlet and Triplet Excited States in Organic Solar Cells
Zhihua Xu and Bin Hu
Adv. Funct. Mater. 18, 2611-2617, 2008
- ⁴ Dissociation Processes of Singlet and Triplet Excitons in Organic Photovoltaic Cells
Zhihua Xu, Yue Wu, and Bin Hu*
Appl. Phys. Lett. 89, 131116 (2006)
- ⁵ Characterization of the Triplet State of Tris(8-hydroxyquinoline)aluminium(III) in Benzene Solution
Hugh D. Burrows, Mariana Fernandes, J. Seixas de Melo, Andrew P. Monkman and Suppiah Navaratnam
J. Am. Chem. Soc. 125, 15310-15311 (2003)
- ⁶ Triplet Enhanced Photovoltaic Response in Organic Solar Cells
Zhihua Xu and Bin Hu, under review in *Appl. Phys. Lett.*
- ⁷ Heavy-metal Structures Effects on Exciton Dissociation in Organic Solar Cells
Zhihua Xu and Bin Hu, to be published
- ⁸ Tuning Magnetic Field Dependence of Electroluminescence in Non-Magnetic Organic Semiconducting Materials
Ming Shao, Liang Yan, and Bin Hu, to be published
- ⁹ Magnetic Field-Dependent Photoluminescence Based on Inter-Molecular Excited States
Liang Yan, Ming Shao, and Bin Hu, to be published